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FOR MORE INFORMATION
Gary Ellis
Department of Polymer Physics and Engineering
Inst. of Polymer Science and Technology
gary@ictp.csic.es

STUDY OF THE MICROSTRUCTURE OF POLYMORPHIC INTERPHASES IN FIBER REINFORCED POLYPROPYLENE COMPOSITES BY SYNCHROTRON IR MICROSPECTROSCOPY AND X-RAY MICRODIFFRACTION

G. Ellis[1], M.A. Gómez[1], C. Marco[1], J. Torre[2], M. Cortázar[2], C. Riekel[3] and P. Dumas[4]

[1]Dpto. Física e Ingeniería, Instituto de Ciencia y Tecnología de Polímeros (CSIC), Spain; [2]Dpto. Ciencia y Tecnología de Polímeros, Facultad de Química, Universidad del País Vasco UPV/EHU, Spain; [3]European Synchrotron Radiation Facility, France; [4]Synchrotron SOLEIL, France

The nature of the fiber-matrix interphase conditions the final properties of fiber-reinforced semicrystalline polymers. Heterogeneous nucleation at the fiber surface can alter the properties of the matrix, thus the understanding and control of the crystalline morphology and microstructure of the interphase is fundamental. Spatially resolved information was obtained from an LCP fiber reinforced isotactic polypropylene model composite using two synchrotron-based methods; infrared microspectroscopy and microfocus x-ray diffraction. The combination of IR microspectroscopy with spatially resolved crystallographic information, obtained for the first time from a polymorphic fiber–matrix interphase, confirms a generally accepted model based on morphological evidence.

Fiber-reinforcement is one of the most important strategies to improve the application properties of both commodity and engineering polymers. With an annual production of more than 2.5 billion pounds, and a spectacular growth rate, the U.S. fiber-reinforced polymer (FRP) market is expected to surpass the $6-billion mark in the next few years. Many everyday items employ FRPs, from automobiles, boats, and sports goods to civil engineering structures and biomedical devices. While glass fiber thermosets occupy more than 60 percent of the market, one of the main growth areas is thermoplastic resins, including polypropylene, and the use of alternative fiber types for reinforcement. Thermotropic liquid crystal polymer (LCP) fibers are interesting because of their superior mechanical properties, excellent melt flow properties, reduced machine wear and processing costs, good recyclability, and low density almost half that of glass fibers. This is important for the design of strong, lightweight components.

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LCP fibers can induce heterogeneous nucleation in isotactic polypropylene (iPP) with a high density of nucleation sites at the fiber surface, and the habitual three-dimensional spherulitic growth is impeded due to overcrowding. Crystalline growth takes place perpendicular to the fiber surface generating a *transcrystalline* (*TC*) layer around the fiber, in which both the elastic and tensile moduli are improved. Various crystalline polymorphs can be observed in iPP; the thermodynamically more stable monoclinic α-modification predominates, whereas crystallization of the less stable trigonal β-modification requires specific conditions such as thermal gradients, shear stresses, or the presence of specific β nucleating agents. Generally when fiber-reinforcement generates a *TC* morphology, the α-form of iPP is observed, and the *TC* β-phase is rare. However, there is much interest in the mechanical properties of the β-phase, particularly improved toughness and impact strength, although the mechanisms that generate the β-phase and the exact relationship between the presence of *TC* morphologies and the final properties of the material are still much debated issues.

Shear stress can also generate β-phase *TC-like* iPP around fibers, and a *cylindritic* crystalline superstructure is developed, differentiating it from *TC* structures. The most important evidence for this comes from polarized thermo-optical light microscopy that, along with morphological data from SEM and AFM, support the Varga and Karger-Kocsis model: shear produced in the melt by fiber-pulling generates extended chain geometries that give rise to series of α-row nuclei along the fiber surface. At the interface of this thin layer of oriented α-crystals a transition from the α- to the

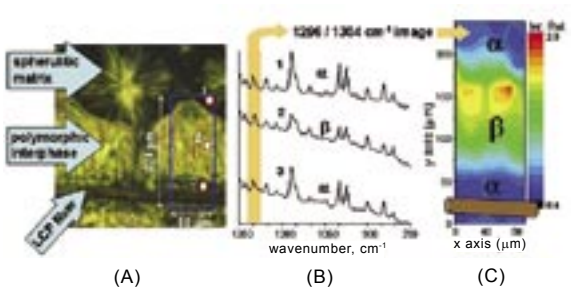
β-phase takes place, giving rise to the formation of the β-cylindritic crystalline superstructure.

Our main goal was to obtain direct structural information from the fiber-matrix interphase. We have studied samples where fiber-pulling at 140 ºC generated shear in the polymer melt, and after isothermal crystallization and subsequent cooling to room temperature, selected regions of the samples were examined using both infrared microspectroscopy and wide-angle x-ray microdiffraction.

Mapping relative IR band intensities at specific sampling geometries in the highly polarized synchrotron beam allows us to differentiate between the two crystalline polymorphs (**Figure 1**), and a false-color image of the marked area clearly shows evidence of a layer of α-phase iPP around the fiber. Unequivocal identification depends on the relative orientation of the polymer chains with respect to the polarization axis of the synchrotron beam.

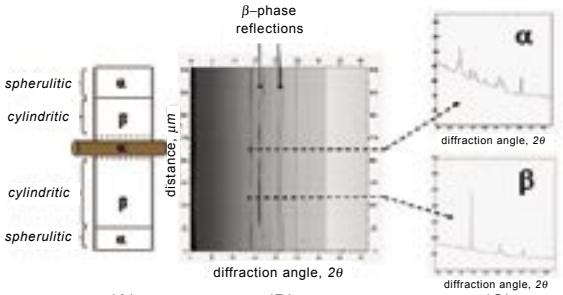
This is confirmed with wide-angle x-ray microdiffraction experiments (**Figure 2**). A 3 μm diameter x-ray beam was scanned through the interphase region perpendicular to the fiber axis in 5 μm steps. The observation of the β-cylindritic layer and a highly ordered α-phase iPP close to the fiber **(Figure 2C)** confirms the spectroscopic evidence.

The presence of a thin layer close to the sheared fiber corresponding to the α-phase has been unequivocally confirmed by both synchrotron IR microspectroscopy and x-ray microdiffraction. We hope further high spatial resolution studies of the chain geometry in the transition zone will provide more information on the mechanisms involved in the formation of the highly ordered β-phase.



(A) (B) (C)

Figure 1. Synchrotron infrared microspectroscopy. (A) Polarized light microscopy of polymorphic iPP interphase, (B) IR spectra recorded through an 8 μm aperture at positions marked, and (C) false-color IR imaging of the interphase region using relative band intensities indicated. The LCP fiber position is also shown.



(A) (B) (C)

Figure 2. Synchrotron x-ray microdiffraction. (A) Schematic of sampled region showing original position of LCP fiber, (B) integrated intensities of x-ray patterns obtained from a 400 μm line-scan, and (C) diffraction patterns from positions marked.